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TITLE: **MANUFACTURING METHOD OF SEMICONDUCTOR DEVICE**

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1. TITLE OF INVENTION

Manufacturing method of semiconductor device

2. CLAIMS

[Claim 1]

A manufacturing method of semiconductor device, which forms a transparent electrode, amorphous silicon type semiconductor layer, and a back surface electrode on a substrate with a pattern and in this order, wherein the patterning is characteristically carried out by coating an etching solution on the desired location of the amorphous silicon type semiconductor layer and (or) back surface electrode layer.

[Claim 2]

The manufacturing method described in Claim 1, wherein the said coating of the etching solution is carried out by a nozzle.

[Claim 3]

The manufacturing method described in Claim 1, wherein the said coating of the etching solution is carried out by an etching solution coating material immersed into the etching solution.

[Claim 4]

The manufacturing method described in Claim 3, wherein the said etching solution coating material is a line type body.

[Claim 5]

The manufacturing method described in Claim 3, wherein the said etching solution coating material is a sheet type body.

[Claim 6]

The manufacturing method described in Claim 1, wherein the said coating of the etching solution is carried out by an etching pen.

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[Claim 7]

The manufacturing method described in Claim 1, wherein the etching solution used for the etching of the amorphous silicon type semiconductor layer is either KOH aqueous solution or NaOH aqueous solution.

[Claim 8]

The manufacturing method described in Claim 1, wherein the back surface electrode is Al; and the etching solution is: the mixed solution of phosphoric acid, acetic acid, nitric acid, and pure water; diluted hydrochloric acid; KOH aqueous solution or iron (III) chloride; or the mixed solution of concentrated hydrochloric acid and pure water.

[Note from the Translator- The etching solution type may be also interpreted as "the mixed solution of phosphoric acid, acetic acid, nitric acid, and pure water; diluted hydrochloric acid; or the mixed solution of KOH aqueous solution or iron (III) chloride, concentrated hydrochloric acid and pure water".]

[Claim 9]

The manufacturing method described in Claim 1, wherein the back surface electrode is Cr; and the etching solution is the mixed solution of cerium (IV) ammonium nitrate, perchloric acid, and pure water.

[Claim 10]

The manufacturing method described in Claim 1, wherein the back surface electrode is Ag; and the etching solution is: the mixed solution of chromic anhydride, concentrated sulfuric acid, and water; iron (III) nitrate aqueous solution; the mixed solution of ammonia water and hydrogen peroxide solution; or diluted nitric acid.

3. DETAILED EXPLANATION OF INVENTION

[Industrial Application Fields]

The present invention relates to the manufacturing method of the semiconductor device. Further in details, the present invention relates to the manufacturing method of the semiconductor device in which the patterning is carried out by a simple method.

[Conventional Techniques and Problems Solved by the Invention]

Conventionally, the patterning of the amorphous silicon type semiconductor layer and back surface electrode has been carried out by utilizing an energy beam, such as a laser beam, for the integration.

However, when the laser patterning is carried out for the amorphous silicon type semiconductor layer, there are problems: the damage on the transparent electrode may impair the solar cell performance, or the contact resistivity between the transparent electrode and back surface electrode at the laser scribed section may change (increase in the resistivity) with time. Further, the laser patterning of the back surface electrode disadvantageously fails to achieve the stable production due to a high working difficulty. Therefore, the other methods such as the etching method or lift-off method must be employed. In this case, other problems, such as the increase in the treatment process

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number and the increase in the manufacturing cost and the yield reduction due to the decrease in the productivity, occur. Further, even at either of the said cases, the patterning is carried out after forming the amorphous silicon type semiconductor layer or back surface electrode, therefore, the manufacturing cost has increased with the increase in the process number.

The present invention is based on the said problems and aims to offer the manufacturing method of the semiconductor device which can reduce the treatment process steps during the etching method and increase the productivity.

[Methods to Solve Problems]

The manufacturing method of semiconductor device of the present invention is the semiconductor device manufacturing method, which forms a transparent electrode, amorphous silicon type semiconductor layer, and a back surface electrode on a substrate with a pattern and in this order, wherein the patterning is characteristically carried out by coating an etching solution on the desired location of the amorphous silicon type semiconductor layer and (or) back surface electrode layer.

[Execution Examples]

Then, the manufacturing method of the semiconductor device of the present invention is interpreted.

On a substrate such as a sheet glass, a transparent electrode made of tin oxide and so on is formed by a plasma CVD method, sputtering method, or the vapor deposition method, and the said transparent electrode is patterned with the laser scribe method and so on. Then, the said substrate is immobilized on a CVD tray and an amorphous silicon type semiconductor layer is formed. The said amorphous silicon type semiconductor layer is formed in the order of, for example, p layer, i layer, and n layer by the plasma CVD method and so on, under the ordinary condition.

On the desired location of the amorphous silicon type semiconductor layer obtained as above, the etching solution is coated.

The coating of the etching solution is carried out by a nozzle to spray the etching solution, line type body such as a wire or sheet type body such as a metal piece (below these are referred to as "etching solution coating material") immersed into the etching solution, or by an etching pen.

When the etching solution is coated by a nozzle, the nozzle is installed to the desired position of the amorphous silicon type semiconductor layer, and the etching solution is sprayed while moving the said nozzle. The etching solution can be similarly coated on by moving the substrate, instead of moving the nozzle.

The nozzle diameter is appropriately designed according to the formed pattern line, however, it is desirably from 0.01 to 1.0 mm, more preferably from 0.02 to 0.3 mm,

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by considering the increase in the effective area. Further, the distance between the substrate and the nozzle is desirably from 0.5 to 10 mm, more preferably from 1 to 2 mm, for the uniform coating the etching solution.

The device to spray the etching solution may be any type as long as the etching solution can be sprayed from the nozzle. For example, the etching jet can be used. This etching jet is the ink jet utilizing the etching solution, in place of ink.

When the etching solution is coated by using the etching solution coating material immersed into the etching solution, the etching solution coating material is pressed against the desired location of the amorphous silicon type semiconductor layer. As the measure to press the etching solution coating material, the method to press the wire fine line or metal made thin sheet on the substrate in close contact, for example, may be used.

When the etching solution is coated by using an etching pen, the pen tip of the etching pen is installed to the desired location of the amorphous silicon type semiconductor layer at a height with a light touching. Then, the etching solution is released while the said pen is moving. The etching solution can be similarly coated on by moving the substrate, instead of moving the etching pen.

The pen tip diameter of the etching pen is appropriately designed according to the formed pattern line, however, it is desirably from 0.05 to 1.0 mm, more preferably from 0.1 to 0.5 mm, by considering the increase in the effective area (the decrease in the inert region).

As the etching solution for the amorphous silicon type semiconductor layer, either KOH aqueous solution or NaOH aqueous solution can be used. The concentration for the KOH and NaOH aqueous solution is desirably from 1 to 50 wt%, more preferably from 10 to 30 wt%, from the view points of the prevention of the excessive removal of the amorphous silicon film and the easy control of the etching time. Further, the temperature of the KOH and NaOH aqueous solution is desirably from 10 to 40 °C, more preferably from 20 to 30 °C, from the view points of the prevention of the excessive removal of the amorphous silicon type semiconductor film and the maintenance of the etching solution viscosity within a certain range.

When the etching is carried out by installing the substrate on a hot plate, the substrate is heated uniformly and the etching is activated, thus the etching can be carried out uniformly and the etching speed is improved. The substrate temperature is desirably from 10 to 100 °C, more preferably from 20 to 50 °C, from the view points of the prevention of the excessive removal of the amorphous silicon film and the easy control of the etching holding time.

After coating of the etching solution on the amorphous silicon type semiconductor layer, the etching is carried out by holding for a certain time period. This

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holding time is from 5 to 15 minutes at room temperature or from 30 seconds to 5 minutes at 40 °C atmospheric temperature, by considering the etching speed.

After the completion of the etching, the whole substrate is washed with pure water and dried.

After patterning the amorphous silicon type semiconductor layer as above, the said substrate is immobilized to, for example, a sputter tray, and the back surface electrode is formed by sputtering the metal such as Al, Cr, Ag, and so on. Then, the patterning of the back surface electrode is carried out.

The patterning of the back surface electrode may be carried out by the similar procedure as the amorphous silicon type semiconductor layer, except the composition of the etching solution is different from that used for the amorphous silicon type semiconductor layer.

When Al, for example, is used as the back surface electrode, the etching solution may utilize the mixed solution of phosphoric acid, acetic acid, nitric acid, and pure water. One example of the volume ratio for the said mixed solution is 16 : 2 : 1 : 1 in the order of phosphoric acid, acetic acid, nitric acid, and pure water. This volume ratio may be appropriately selected according to the film thickness for the whole Al and desired pattern line width. For example, when the Al film thickness is 5000 Å and pattern line width is 0.25 mm, the mixed solution having the volume ratio of 16 : 2 : 1 : 5 in the order of phosphoric acid, acetic acid, nitric acid, and pure water, is desirably used. The selection of the mixed solution temperature may be done similarly as the patterning of the said amorphous silicon type semiconductor layer. The holding time after coating of the etching solution is desirably from 0.5 to 15 minutes, more preferably from 0.5 to 3 minutes, in order to prevent the excessive removal of the Al film. Further as the etching solution, diluted hydrochloric acid; KOH aqueous solution or iron (III) chloride; or the mixed solution of concentrated hydrochloric acid and pure water [**Note from the Translator-** The etching solution type may be also interpreted as "diluted hydrochloric acid; or the mixed solution of KOH aqueous solution or iron (III) chloride, concentrated hydrochloric acid and pure water".] may be suitably used, in addition to the said mixed solution.

When the whole substrate is heated on a hot plate for the uniform etching and the improved etching speed, the temperature for the whole substrate is desirably maintained from 10 to 100 °C at room temperature and from 20 to 50 °C at the 40 °C atmospheric temperature from the view points of the prevention of the excessive Al film removal and the easy control of the etching holding time.

When the back surface electrode is either Cr or Ag, the patterning can be carried out similarly to the Al electrode, except the etching solution is different from that used for the Al electrode.

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In other words, the composition of the Cr electrode etching solution may comprise 20 to 30 ml of perchloric acid and 300 to 1000 ml of pure water against 100 g of cerium (IV) ammonium nitrate. One example of the desirable composition comprises 28 ml of perchloric acid and 400 ml of pure water.

Further, the composition of the Ag electrode etching solution may be the mixed solution comprising 30 to 50 g of chromic anhydride, 10 to 30 ml of concentrated sulfuric acid, and 1000 to 5000 ml of pure water, or 30 to 60 wt% iron (III) nitrate aqueous solution. One example of the desirable composition is the mixed solution of 40 g of chromic anhydride, 20 ml of concentrated sulfuric acid, and 2000 ml of pure water, or 55 wt% iron (III) nitrate aqueous solution.

Here, when a double layer structured back surface electrode is formed in order to prevent the diffusion of the metal constructing the back surface electrode into the amorphous silicon type semiconductor layer, for example, when Cr (20 to 100 Å) / Al (1000 to 10000 Å) is used, the etching can be carried out by one step by using the common etching solution such as the diluted hydrochloric acid or diluted sulfuric acid.

For all the other metal electrodes, the patterning can be carried out by the similar method as this.

In the interpretation above, the manufacturing method of the present invention is applied when the amorphous silicon type semiconductor layer and the back surface electrode are formed. Here, the manufacturing method of the present invention is characterized by the employment of at least one patterning, therefore, it is possible to pattern one by the present invention and to pattern the other by another method.

Then, the manufacturing method of the semiconductor device of the present invention is interpreted based on the example, however, the present invention is not limited to this example.

Example

On a blue sheet glass having a 2.0 mm thickness and 150 x 440 mm size, a tin oxide transparent electrode with 6000 Å was formed by the plasma CVD method. The obtained transparent electrode was separated into the desired pattern by using a laser beam. Then, 150 Å of p type amorphous silicon layer (substrate temperature of 130 °C and pressure of 1.0 Torr), 6000 Å of i type amorphous silicon layer (substrate temperature of 180 °C and pressure of 0.5 Torr), and 300 Å of n type micro- crystalline silicon layer (substrate temperature of 180 °C and pressure of 1.0 Torr) were formed on the transparent electrode side in this order by the glow discharge decomposition method.

Then, a nozzle having a 0.1 mm diameter and the mechanism to automatically spray the etching solution was arranged so that the distance between the nozzle and the substrate was 2 mm. And by moving the nozzle, the etching solution for the

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amorphous silicon type semiconductor, KOH 10 wt% aqueous solution, was sprayed from the nozzle on the section of the amorphous silicon type semiconductor layer to be separated. The solution temperature of the etching solution was 20 °C. After spraying the etching solution, the substrate was held for 10 minutes, and then washed with pure water and dried. This etched section (patterned line) was observed. There was no residue of the amorphous silicon type semiconductor layer and the transparent electrode was uniformly exposed. Further, the minimum pattern width of the section exposing the transparent electrode was measured by using the precision projector. The average number for 17 lines was 0.2 mm.

Then, for the obtained amorphous silicon type semiconductor separated substrate, an Al back surface electrode with 5000 Å thickness was formed by using a magnetron sputtering device (Ar pressure of 1×10^{-3} and the substrate temperature of 80 °C). Then, the etching pen having a 0.1 mm pen tip was filled with 5 ml of Al etching solution with about 20 °C of solution temperature, in other words, the mixed solution of phosphoric acid, acetic acid, nitric acid, and pure water (compositional ratio of 16 : 2 : 1 : 1). The height of this etching pen was adjusted so that it became in contact with the substrate formed with the Al back surface electrode and immobilized to the X - Y plotter. Then by moving the X - Y plotter, the etching solution was coated on the Al electrode to be separated. After coating with the etching solution, the substrate was held for 10 minutes, and then washed with pure water and dried. This etched section (patterned line) was observed. There was no Al connecting sections. Further, the minimum pattern width of the section exposing the amorphous silicon type semiconductor layer was measured by using the precision projector. The average number for 17 lines was 0.25 mm.

By the procedure above, the solar cell, in which 18 photovoltaic elements are serially connected on one substrate, was prepared and the performance was measured by the AM- 1.5 approximate pulse simulator. The results are shown in table 1

Comparison Example

The transparent electrode was patterned by the similar procedure as in Example, and the amorphous silicon type semiconductor layer was formed. The separation of the amorphous silicon type semiconductor layer was carried out by using YAG laser. Further, the Al back surface electrode was formed under the condition similar to the Example, and then the separation of the Al back surface electrode was carried out by the ordinary chemical etching.

The performance of the obtained solar cell was measured by the similar method as the Example. The measurement results are shown in Table 1.

Table 1

	Isc (mA)	Vo.c (V)	F. F (%)	Max. output (Wp)
Example	405	16.2	63	4.13
C. Example	400	16.0	61	3.90

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Table 1 apparently indicates that the solar cell obtained by the present invention possesses the similar or better performance than that obtained by the conventional techniques.

[Effects of Invention]

As interpreted above, the manufacturing method of the semiconductor device of the present invention enables the perfect patterning with a simple measure, thus the manufacturing cost can be reduced and the product yield improves. Further, it offers the effect to eliminate the complex processes such as the resist coating and resist removal necessary in the ordinary etching method.